CHAPTER 1

INTRODUCTION

1.1 General Introduction

Chemical process industry is a large industry with a global turnover of US $1400 billion per year (Roland and Kleinschmit, 1996). It has been recognized that the status of chemical process industry is a reliable indicator of the country's state of industrialization. It is well known that the chemical process industry is mainly based on catalytic processes. More than 90% of all chemical products manufactured involve at least one catalytic step, mostly even several catalytic procedures (Hölderich *et al.,* 1997). Zeolite acid catalysts have a wide application in industrial processes such as alkylation, isomerization, amination, cracking and etc (Tanabe and Hölderich, 1999). According to them, zeolites are the highest number of catalyst used in industrial processes. The utilization of zeolites as catalysts in industrial processes occupies 40%, followed by the oxides, complex oxides and ion-exchange resins.

The ability of zeolites as catalysts in organic processes has been investigated by many researchers. Zeolite Beta is a typical example of the zeolite with high activity in fine chemical reactions. Zeolite Beta has proven to be a reactive acid catalyst in many organic processes such as alkylation (Cheralathan *et al.,* 2003; Chiu *et al.,* 2004), acylation (Casagrande *et al.,* 2000) and various hydrocarbon reactions (Absil and Hatzikos, 1998). Zeolites are employed as an alternative heterogeneous catalyst instead of homogeneous catalysts particularly in Friedel-Crafts reaction since it is more efficient and environmentally-friendly which can eventually reduce plant corrosion and eliminate environmental problems. The key opportunity for the use of zeolites as catalysts relies on their unique pores which can control the selectivity of the reaction. Zeolites possess acid sites on the surface which can catalysed reaction such as Friedel-Crafts. The acid sites in zeolites are linked to tetrahedral aluminium atoms in the framework of the zeolite (Zaiku *et al.,* 2002). Therefore the acidity depends on the amount of aluminium framework.

1.2 Research Background

Friedel-Crafts alkylation of aromatics is one of the most significant basic reaction in organic chemistry and of great importance in synthesizing fine chemicals. Some of these chemicals are used in the production of antioxidants (Narayanan and Murthy, 2001; Zhang *et al.*, 1998), intermediates for polyester fibers, engineering plastics, and liquid crystalline polymers for electronic and mechanical devices and films (Ahedi *et al.,* 2003). More specifically, the alkylation of resorcinol with *tert*-butanol is a reaction of practical interest since it produces butyl resorcinol which has potential uses as antioxidants, polymer stabilizers and in the treatment of mitochondrial respiration ailments (Narayanan and Murthy, 2001).

In general, Friedel-Crafts reaction is carried out with classic Lewis acid catalyst such as $AlCl_3$, BF_3 and $TiCl_4$, coupled with strong mineral acids such as HF and H_2SO_4, $Cu(OTf)_2$ and $Sn(OTf)_2$ (Chandra *et al.,* 2002). However the present use of conventional Lewis acid catalysts such as $AlCl_3$ courses a number of problems. First, the use of greater than stoichiometric amounts of the catalyst are needed, due to the configuration of a complex between the product and the catalyst. Second, the following hydrolysis of the catalysts leads to the loss of the catalyst as well as the problem of the disposal of the catalyst which consequently affects the environment. Therefore, heterogeneous catalysts have been chosen to replace the homogeneous catalysts in Friedel-Crafts reaction. The use of zeolites and other solid acid catalysts as heterogeneous catalysts in the manufacture of chemical intermediates and fine chemicals is gaining much more attention in recent years (Tanabe and Hölderich, 1999).

In this research, we have chosen zeolite Beta to be studied as the catalyst, following the current development in heterogeneous catalysis in Friedel-Crafts reaction. Zeolite Beta has great potential industrial interest because of its high acidity, large pore (5.0-7.0 Å) and peculiar pore systems and high silica content and has a high thermal stability. It is well known that zeolite possesses both Brönsted and Lewis acid sites. The acidity of a zeolite is one of the most important topics in the study of zeolite catalysis. The acid sites in zeolites are linked to the tetrahedral aluminium atoms in the framework of the zeolite (Zaiku *et al.,* 2002). Studies have shown that the amount of Brönsted and Lewis acid determine the selectivity of Friedel-Crafts reaction (Narayanan and Muthy, 2001; Narayanan and Sultana, 1998; Nivarthy *et al.,* 1998; Yadav and Doshi, 2003). Therefore, in this study the acidity of zeolite Beta will be modified by varying the Si/Al ratio of the framework as well as introducing niobium oxides as a support metal into zeolite Beta lattice.

1.3 Research Objectives

The objectives of this study are:

1) To synthesize zeolite Beta at different Si/Al ratios.
2) To modify the acidity of zeolite Beta by introducing niobium oxide
3) To determine the acidity of the modified zeolite beta.
4) To test the reactivity of the catalysts in Friedel-Crafts alkylation of resorcinol with *tert*-butanol.

1.4 Scope of Research

In this research, zeolite Beta was first synthesized using white rice husk ash (RHA) as silica sources. Zeolite Beta was synthesized with various SiO_2: Al_2O_3 molar ratios of the initial gel to obtain zeolite Beta with different Si/Al ratios framework. The acidity of zeolite Beta was further modified by introducing niobic acid as niobium oxide precursor through wet impregnation method.

The characterization of the catalysts was performed by using appropriate techniques which include powder X-ray diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), ^{29}Si Magic Angle Spinning (MAS) NMR spectroscopy, UV-Visible Diffuse Reflectance spectroscopy (UV-Vis DR) and nitrogen adsorption-desorption measurement. The acidity measurement of the prepared zeolite Beta catalysts was carried out by Temperature Programmed Desorption (TPD) of ammonia method and pyridine adsorption monitored by Fourier Transform Infrared spectroscopy (FTIR).

The final part in this study was to test the catalytic activity of the prepared catalysts in Friedel-Crafts alkylation of resorcinol with *tert*-butanol. The comparison of reactivity and selectivity of the catalysts in the Friedel-Crafts alkylation has been made between unmodified zeolite Beta and modified zeolite beta. The reaction was performed in a batch reactor and the product was analysed by gas chromatography (GC) while the identification of the products was carried out by using Gas Chromatography-Mass Spectrometry (GC-MS). Lastly, the study of antioxidant properties of the Friedel-Crafts reaction product was conducted by reacting the sample with 1,1-diphenyl-2-picryl-hydrazyl (DPPH) radical and the activity was measured using Electron Spin Resonance (ESR) method.